Supporting Information

Effect of the Hydrofluoroether Cosolvent Structure in Acetonitrile-Based Solvate Electrolytes on the Li^+ Solvation Structure and Li–S Battery Performance

Minjeong Shin,[†,‡,#] Heng-Liang Wu,[†,‡,#] Badri Narayanan,[†,∥] Kimberly A. See,[†,‡] Rajeev S. Assary,[†,∥] Lingyang Zhu,[‡] Richard T. Haasch,[§] Shuo Zhang,[†,⊥] Zhengcheng Zhang,[†,⊥] Larry A. Curtiss,[†,∥] and Andrew A. Gewirth[*,†,‡]

[#] These authors contributed equally to this work.

[†] Joint Center for Energy Storage Research, 9700 South Cass Avenue, Argonne, Illinois 60439, United States

[‡]Department of Chemistry and [§]Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

[∥]Materials Science Division and [⊥]Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Corresponding Author:

*Email: agewirth@illinois.edu

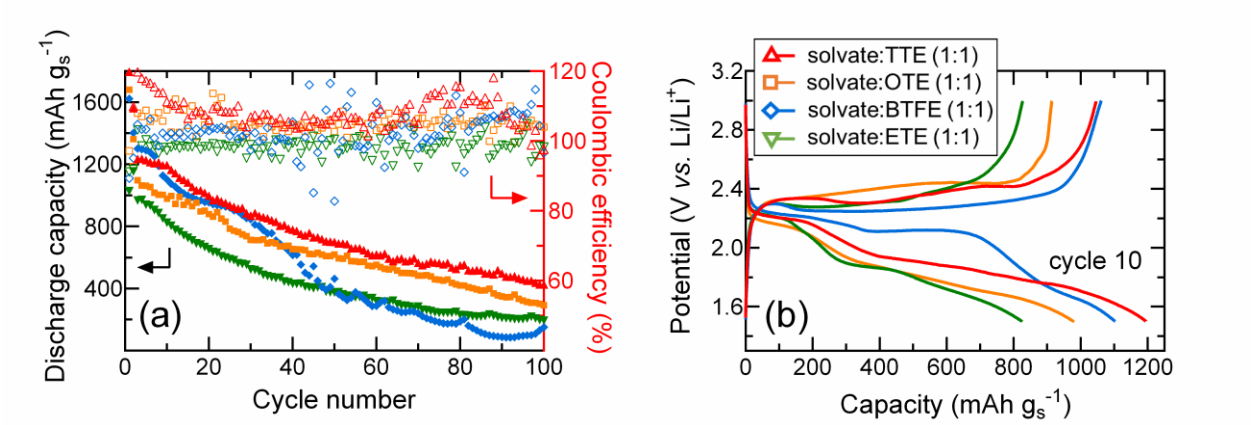

Figure S1. (a) Electrochemical performance of Li–S cells prepared with a Li metal anode, S@CMK–3 cathode, and a $(MeCN)_2$–LiTFSI solvate electrolyte diluted with HFEs at a volume ratio of 1:1 (solvate:HFE). The cells are cycled between 1.5 and 3.0 V at 0.05 C for the first two cycles and 0.1 C for the following cycles. The Coulombic efficiency (CE) shown here is the discharge efficiency and was determined by CE = $Q_{discharge}/Q_{charge} \times 100$. (b) Corresponding charge and discharge curves for cycle 10. The Li–S cell cycling was performed at room temperature.

Table S1. Physicochemical properties of the $(MeCN)_2$–LiTFSI solvate electrolyte diluted with HFE at a 1:1 volume ratio.

Electrolyte	**mole ratio of MeCN:LiTFSI:HFE**	**Density (g mL^{-1})**	**LiTFSI concentration (M)**	**Viscosity (cP)**
solvate:TTE (1:1)	2 : 1 : 1.636	1.476	1.971	9.837
solvate:OTE (1:1)	2 : 1 : 1.212	1.546	2.003	15.62
solvate:BTFE (1:1)	2 : 1 : 1.893	1.420	1.989	5.734
solvate:ETE (1:1)	2 : 1 : 2.010	1.334	2.013	4.739

Table S2. Vibrational frequencies and assignments of Raman modes in $(MeCN)_2$–LiTFSI solvate electrolyte diluted with HFEs.

	peak label		a	a'	b	b'	c	c'
assignment	species		$TFSI^-$	$TFSI^-$	MeCN	MeCN	MeCN	MeCN
	modes		ν_s(S–N–S), $\delta(SO_2)$, $\delta(CF_3)$	mode a, coordinated to Li^+	ν_s(C≡N)	mode b, coordinated to Li^+	ν_s(C–H)	mode c, coordinated to Li^+
	ref		1-4	2, 5-6	7-8	1, 5-6, 9	7-8	5
Raman shift (cm^{-1})	**$(MeCN)_2$–LiTFSI (solvate)**		742	749	2256	2278	2294	2308
	solvate:TTE vol. ratio	2:1	742	749	2257	2279	2295	2309
		1:1	742	750	2257	2280	2296	2309
		1:2	742	750	2257	2280	2296	2309
	solvate:OTE vol. ratio	2:1	742	749	2257	2280	2296	2309
		1:1	742	749	2257	2280	2296	2310
		1:2	742	750	2257	2281	2296	2310
	solvate:BTFE vol. ratio	2:1	742	749	2257	2279	2295	2309
		1:1	742	750	2257	2280	2296	2310
		1:2	742	750	2257	2281	2296	2310
	solvate:ETE vol. ratio	2:1	742	749	2256	2279	2295	2308
		1:1	742	749	2256	2279	2295	2309
		1:2	742	749	2256	2280	2296	2309

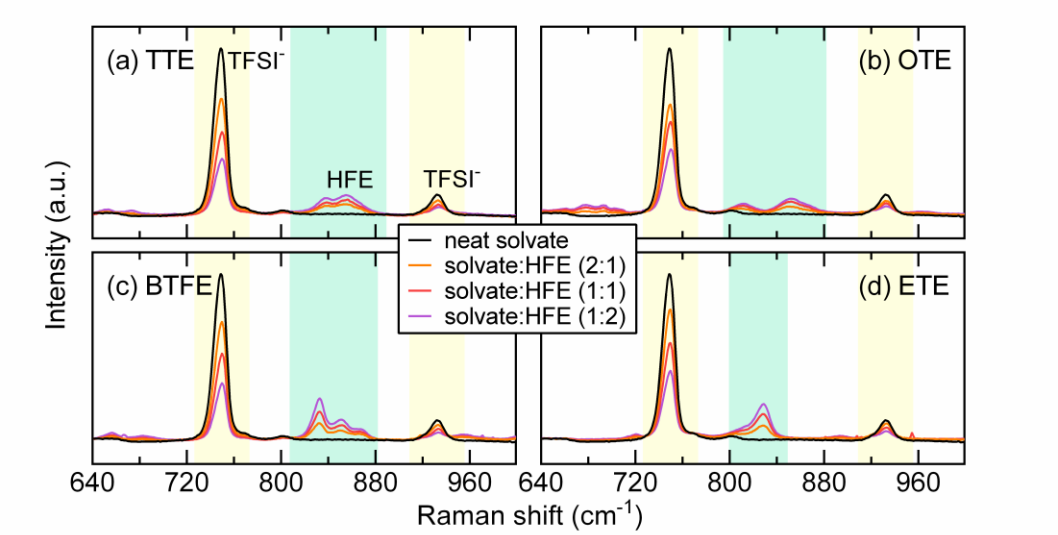

Figure S2. Low wavenumber region Raman spectra of neat $(MeCN)_2$–LiTFSI solvate electrolyte diluted with (a) TTE, (b) OTE, (c) BTFE, and (d) ETE with volume ratios of 2:1, 1:1, and 1:2 (solvate:HFE). The region highlighted with yellow shows $TFSI^-$ bands and the region highlighted with green shows HFE bands.

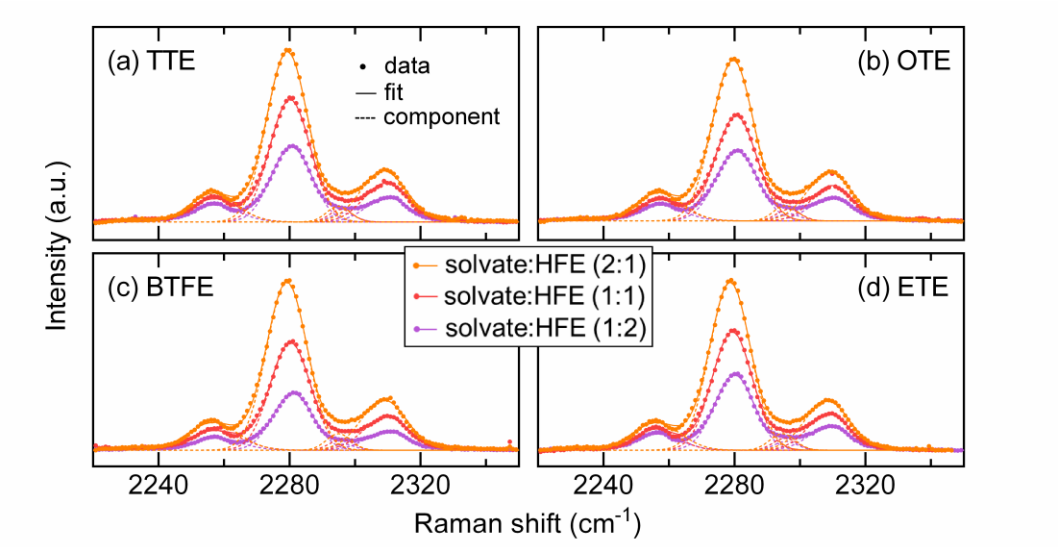

Figure S3. High wavenumber region Raman spectra of neat $(MeCN)_2$–LiTFSI solvate electrolyte diluted with (a) TTE, (b) OTE, (c) BTFE, and (d) ETE with volume ratios of 2:1, 1:1, and 1:2 (solvate:HFE). The spectra are fit with four component using Gaussian profiles.

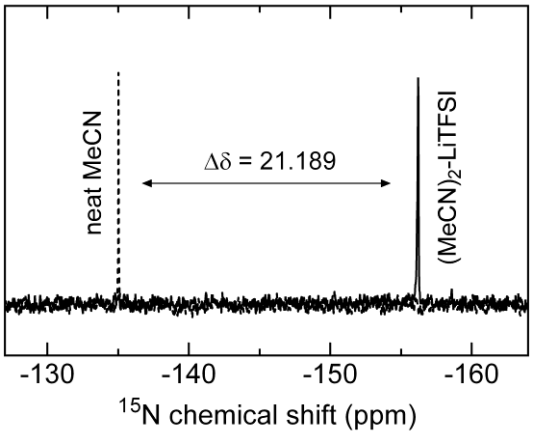

Figure S4. ^{15}N NMR spectra of neat MeCN and $(MeCN)_2$–LiTFSI as indicated. The resonance of the ^{15}N nucleus shifts upfield by 21.189 ppm as a result of LiTFSI addition to the MeCN. ^{15}N chemical shifts were referenced to NH_4NO_3-$^{15}N_2$ in D_2O.

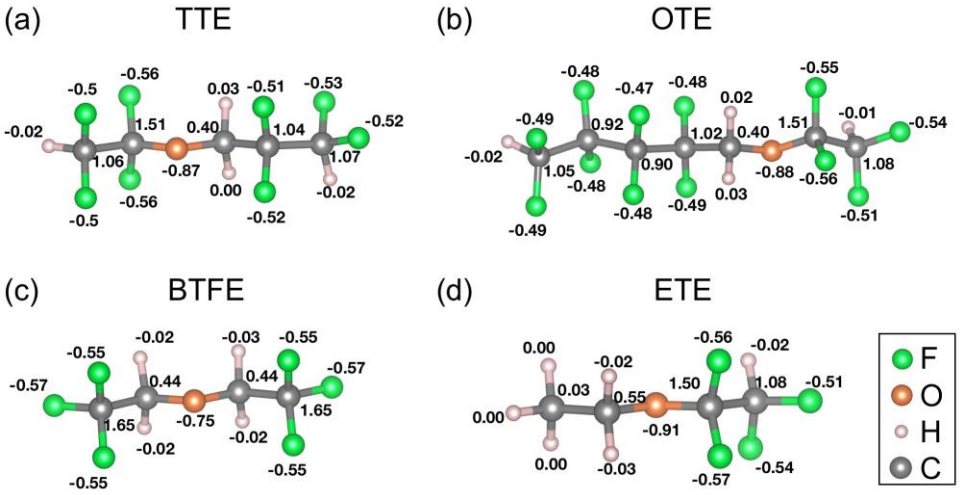

Figure S5. Atomic partial charges of (a) TTE, (b) OTE, (c) BTFE, and (d) ETE derived from quantum chemical calculations.

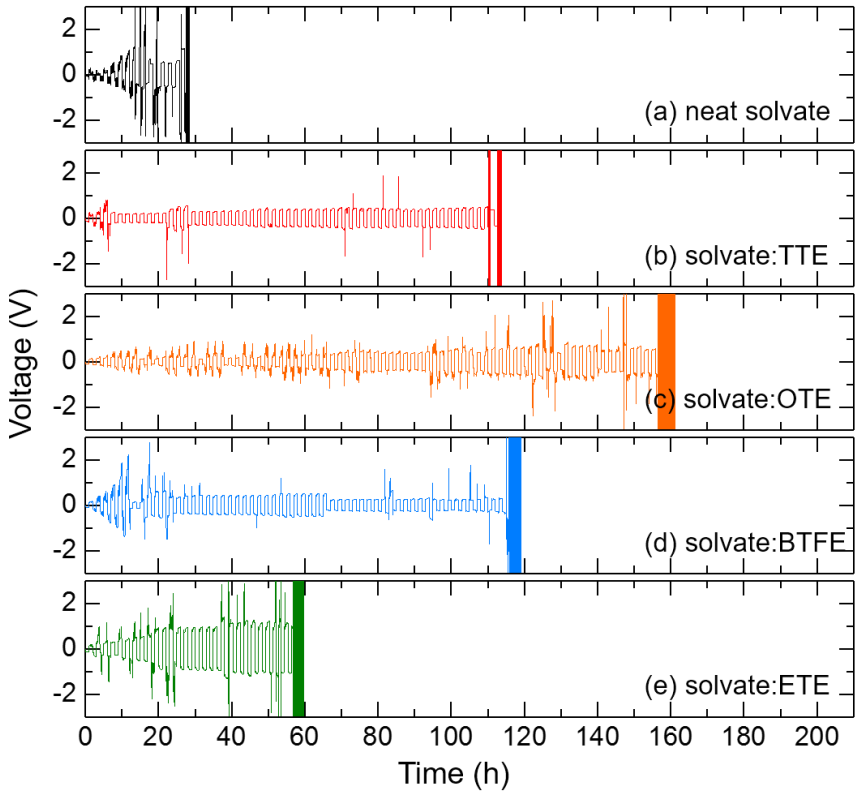

Figure S6. Voltage profiles showing galvanostatic cycling of Li metal plating/stripping at 0.5 mA cm^{-2} in symmetric Li-Li cells with (a) neat $(MeCN)_2$–LiTFSI solvate, (b) solvate:TTE (2:1), (c) solvate:OTE (2:1), (d) solvate:BTFE (2:1), and (e) solvate:ETE (2:1) electrolytes. The amount of Li cycled was 0.5 mAh cm^{-2} per cycle.

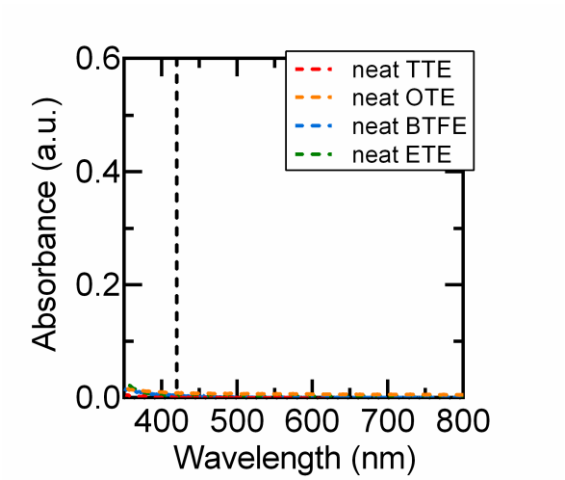

Figure S7. UV-vis spectra of HFE-only solutions saturated with "Li_2S_8".

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